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(54) Title: ZINC POWDER FOR ALKALINE BATTERIES

(57) Abstract

.0001-.0095 Al

A powder for alkaline batteries consists of: either (1), 1-95 ppm Al, one of 0.001-2 % Bi, 0.005-2 % In and 0.003-2 % Pb, and optionally 0.003-2 % Ca; or (2), 1-95 ppm Al, 0.001-2 % Bi, 0.005-2 % In and optionally 0.003-2 % Ca; or (3), 1-95 ppm Al, one of 0.001-2 % Bi and 0.005-2 % In, 0.003-2 % Pb and optionally 0.003-2 % Ca; or (4), 1-1000 ppm Li, at least one of 0.001-2 % Bi and 0.005-2 % In, and optionally 0.003-2 % Ca; or (5), 1-1000 ppm Li, 0.003-2 % Pb, 0.003-2 % Ca and optionally 0.005-2 % In; or (6), 1-1000 ppm Li, 0.001-2 % Bi, 0.003-2 % Pb and optionally at least one of 0.005-2 % In and 0.003-2 % Ca; or (7), 1-95 ppm Al, 1-1000 ppm Li, at least one of 0.001-2 % Bi, 0.005-2 % In and 0.003-2 % Pb, and optionally 0.003-2 % Ca; and for the rest of zinc and the unavoidable impurities present in the aforesaid metals, being excluded indium bearing powders with 50 ppm Al according to the combinations (1) and (3) unless these powders contain calcium.

1) .0001-.0095 Al

.001-2 Bi or .005-2 In or .003-2 Pb

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ZINC POWDER FOR ALKALINE BATTERIES

The present invention relates to an aluminium- and/or lithium-bearing zinc powder for alkaline batteries.

Aluminium-bearing zinc powders are known from EP-A-0427315. In this document protection is asked for a zinc base powder for alkaline batteries, characterized in that it contains 0.005-2% aluminium as well as
either 0.0001-0.01% REM, REM being a rare earth metal or a mixture of rare earth metals ;
or, besides zinc and unavoidable impurities, only 0.0001-2% of at least one of the elements indium and REM ;
or, besides zinc and unavoidable impurities, only 0.003-2% bismuth and 0.0001-2% of at least one of the elements indium and REM ;
or, besides zinc and unavoidable impurities, only 0.005-2% lead and 0.0001-2% of at least one of the elements indium and REM ;
or, besides zinc and unavoidable impurities, only 0.005-2% lead, 0.003-2% bismuth and 0.0001-2% of at least one of the elements indium and REM.
The first example in this document relates to a powder that is made by atomizing a molten bath with the following composition : 220 ppm Al, 5 ppm La, 12 ppm Ce, 500 ppm Pb, 54 ppm In, the rest being thermally refined zinc. The second example relates to a powder made by atomizing a molten bath with the following composition : 600 ppm Al, 500 ppm Pb, 500 ppm Bi, 100 ppm In, the rest being thermally refined zinc. All other given examples concern powders having aluminium contents going from 0.03 up to 0.06% (all percents given herebefore and hereafter are percents by weight).
The powders according to these examples have in common with each other that they contain at least about 220 ppm Al and that they have a good resistance to corrosion in the electrolyte of the battery before and after partial discharging of the battery. However, they have a drawback in that they may cause a short circuit in certain types of batteries, among others the LR6-type and smaller types.

The aim of the present invention is to provide an aluminium- and/or lithium-bearing zinc powder for alkaline batteries, which does not cause, or causes to a much lesser extent than the powders according to the examples of EP-A-0427315, a short circuit and which nevertheless has a sufficient resistance to corrosion.

The powder according to the invention is characterized in that it consists of

either (1), 1-95 ppm Al, one of 0.001-2% Bi, 0.005-2% In and 0.003-2% Pb, and optionally 0.003-2% Ca ;

or (2), 1-95 ppm Al, 0.001-2% Bi, 0.005-2% In and optionally 0.003-2% Ca ;

or (3), 1-95 ppm Al, one of 0.001-2% Bi and 0.005-2% In, 0.003-2% Pb and optionally 0.003-2% Ca ;

or (4), 1-1000 ppm Li, at least one of 0.001-2% Bi and 0.005-2% In, and optionally 0.003-2% Ca ;

or (5), 1-1000 ppm Li, 0.003-2% Pb, 0.003-2% Ca and optionally 0.005-2% In ;

or (6), 1-1000 ppm Li, 0.001-2% Bi, 0.003-2% Pb and optionally at least one of 0.005-2% In and 0.003-2% Ca ;

or (7), 1-95 ppm Al, 1-1000 ppm Li, at least one of 0.001-2% Bi, 0.005-2% In and 0.003-2% Pb, and optionally 0.003-2% Ca ;

and for the rest of zinc and the unavoidable impurities present in the aforesaid metals, being excluded indium-bearing powders with 50 ppm Al according to the combinations (1) and (3) unless these powders contain calcium.

Indeed, regarding the aluminium in the powder according to the invention, the applicant has found that powder with a low Al content, in contrast to the powders according to the examples of EP-A-0427315, does not cause or seldom causes, a short circuit in the battery in which it is used. Likewise, the applicant has found, as will be proved further, that a very low Al content suffices to give the powder an adequate resistance to corrosion, particularly after partial or complete discharging of the battery. The other alloying elements (Bi and/or Pb and/or In) give the powder a sufficient resistance to corrosion before discharging. Therefore, the powder is suited to any type of alkaline battery such as LR6, LR14, LR20 and others.
Likewise, the applicant has found that the influence of lithium on the gas evolution after partial or complete discharging is similar with that of aluminium. Both elements can therefore be used separately or together.

Here, the following should be noted :
EP-A-0457354 relates among others to zinc powders for alkaline batteries containing 0.01-1% In, 0.005-0.5% in total of one or two of Pb and Bi and 0.005-0.2% in total of one or more of Li, Ca and Al. Many examples of compositions of powders are given : powders without Al, powders with Al ≥ 0.01% and also powders with 25 ppm Al, which however differ from the powder of the invention in that they contain Ca, In and Bi and optionally Pb. No example is given of a lithium bearing powder. However, it is stated that lithium has the same effect as aluminium. Nothing in this document suggests that there is a short circuit problem with heigher

Al contents and that this problem can be solved, without impairing substantially the corrosion resistance of the powder, by limiting the Al content to 1-95 ppm.
JP-A-62176053 describes amalgamated zinc powders containing 0.001-0.5% In, 0.005-0.5% Pb, 0.005-0.5% Al, 0.005-0.5% of one or more of Tl, Sn, Cd and Ga, 0.0001-0.5% of one or more of Li, Na, K, Rb and Ce and 0.005-0.5% of one or more of Ni, Co and Te. Thus these powders contain at least 6 alloying elements and are moreover amalgamated.
From EP-A-0384975 lithium bearing zinc alloys are known which are used for cups for Leclanché batteries. Lithium is added in order to improve the mechanical strength, a feature which has no significance in the case of zinc powders for alkaline batteries.

The preferred compositions of the powder according to the invention are subject of the enclosed claims 2-22.

An easy way to produce the powder of the invention consists in adding all additives, which should be present in the powder to be produced (Al and for instance In and Bi), to the molten zinc and to atomize the thereby obtained alloy with gas, water or a mixture of both.
One can also atomize molten zinc containing already a part of the additives (for instance Al and Bi), whereafter the remaining additives (for instance In) are deposited on the atomized powder, either by cementation from an aqueous solution, or by physical deposition from a gaseous phase ("Physical Vapour Deposition" or PVD), or by chemical deposition from a gaseous phase ("Chemical Vapour Deposition" or CVD). It is clear that the cementation technique can only be applied if the additives are more electropositive than zinc. When more additives have to be deposited on the atomized powder, they can be deposited simultaneously or separately.
One can also atomize molten zinc as such and then deposit all additives on the atomized powder.
It is also possible to introduce a specific additive partly by alloying with the molten zinc and the remainder by deposition on the atomized powder.
Instead of atomization with gas, water or a mixture of both, any technique which is appropriate to convert a molten metal into a powder can be applied, such as for instance centrifugal atomization or casting and grinding of the casted metal.
In case the desired powder contains additives which can be cemented (for instance In), then still another way to produce the powder consists in preparing a powder with the additives which cannot be cemented and optionally with a part of the additives which can be cemented according to one of the abovementioned methods and making an anode from the thus obtained powder. That anode is introduced in the battery and the additives which can be cemented are added to the electrolyte of the battery, from which they cement on the powder of the anode.

This invention relates therefore not only to a powder such as it is introduced in the battery, but also to a powder such as it is present in the battery.

Example 1

This example proves that zinc base powders according to the invention have a good resistance to corrosion in the electrolyte of the battery after partial discharging of the battery.

There are prepared 7 powders with the following composition : Zn, 500 ppm Pb, 500 ppm Bi, 500 ppm In and respectively 0, 5 ,7 ,16 ,21 ,70 en 280 ppm Al. To this end one starts from thermally refined zinc in molten state to which one adds the alloying elements in the desired amounts.
The thus obtained molten bath is homogenized at 450°C by stirring. The molten alloy is made to flow in a jet of compressed air, thereby producing an alloy powder, the particles of which have substantially the same homogeneous composition as that of the homogeneous molten bath.

The alloy powder is sifted so as to separate thereof the fraction over 500 µm and, as far as possible, the fraction below 104 µm. In this way an alloy powder with a particle size of 104 to 500 µm is obtained.

With the alloy powder one produces batteries of the LR14-type. These batteries are discharged at 2.2 Ohm for 2h. Subsequently on determines at 45°C the quantity of hydrogen which is evolved for 7 days. The results are summarized in the table below.

TABLE

Al-content ppm	gassing rate µl/g day
0	96
5	45
7	30
16	20
21	10
70	11
280	2

These results prove that minor additions of Al reduce already considerably the gassing rate.

Example 2

This example proves that zinc base powders according to the invention have a good resistance to corrosion in the electrolyte of the battery after partial discharging of the battery.

Three powders are prepared with the following composition : Zn, 500 ppm In, 500 ppm Bi and respectively 0, 35 and 70 ppm Al. To this end one proceeds like in example 1.

Batteries of the LR14-type are made with the alloy powder. The batteries are discharged at 2.2 Ohm for 9h. Subsequently one determines at 71°C the hydrogen which is evolved for 7 days. One obtains respectively : 165, 101 and 73 µl/g day.

Example 3

This example proves that zinc base powder according to the invention does not cause any short circuit in the LR6-type battery.

Three powders are prepared with the following composition : Zn, 500 ppm In, 500 ppm Bi and respectively 30, 70 and 325 ppm Al. To this end one proceeds like in example 1.

These powders were supplied to battery-makers for use in batteries of the LR6-type. They have told the applicant that the powder with 325 ppm Al is not suited to that type of battery because it can cause short circuits, whereas the powders with 30 and 70 ppm are suited because they do not cause any short circuit in the same type of battery.

Other typical examples of powder according to the invention have the following composition :

.003 .025

Zn - 30 ppm Al - 250 ppm Bi

Zn - 40 ppm Al - 250 ppm Bi

Zn - 70 ppm Al - 250 ppm Bi alloy(c) (50 ppm claim 1)

Zn - 85 ppm Al - 250 ppm Bi

Zn - 30 ppm Al - 250 ppm Bi - 180 ppm Ca

Zn - 70 ppm Al - 250 ppm Bi - 250 ppm Ca

Zn - 30 ppm Al - 250 ppm Bi - 45 ppm Ca

Zn - 70 ppm Al - 250 ppm Bi - 100 ppm Ca

Zn - 30 ppm Al - 250 ppm Bi - 180 ppm Pb

Zn - 70 ppm Al - 250 ppm Bi - 250 ppm Pb alloy (c)

Zn - 30 ppm Al - 500 ppm Bi

Zn - 40 ppm Al - 500 ppm Bi alloy (c)
Zn - 70 ppm Al - 500 ppm Bi
Zn - 30 ppm Al - 500 ppm Bi - 180 ppm Ca
Zn - 30 ppm Al - 1000 ppm Bi
Zn - 40 ppm Al - 1000 ppm Bi alloy (c)
Zn - 70 ppm Al - 1000 ppm Bi
Zn - 30 ppm Al - 1000 ppm Bi - 180 ppm Ca
Zn - 40 ppm Al - 2300 ppm Bi
Zn - 70 ppm Al - 2300 ppm Bi alloy (c)
Zn - 70 ppm Al - 3000 ppm Bi
Zn - 40 ppm Al - 250 ppm In .004 .025
Zn - 70 ppm Al - 250 ppm In .007 alloy (a) cl. 1+7
Zn - 40 ppm Al - 500 ppm In
Zn - 70 ppm Al - 500 ppm In
Zn - 40 ppm Al - 250 ppm In - 200 ppm Ca
Zn - 70 ppm Al - 250 ppm In - 200 ppm Ca
Zn - 40 ppm Al - 500 ppm In - 200 ppm Ca
Zn - 70 ppm Al - 500 ppm In - 200 ppm Ca
Zn - 30 ppm Al - 2300 ppm Bi - 180 ppm Ca
Zn - 30 ppm Al - 3000 ppm Bi - 180 ppm Ca
Zn - 30 ppm Al - 250 ppm In - 250 ppm Bi
Zn - 40 ppm Al - 250 ppm In - 250 ppm Bi
Zn - 70 ppm Al - 250 ppm In - 250 ppm Bi
Zn - 30 ppm Al - 500 ppm In - 250 ppm Bi
Zn - 40 ppm Al - 500 ppm In - 250 ppm Bi
Zn - 70 ppm Al - 500 ppm In - 250 ppm Bi
Zn - 30 ppm Al - 500 ppm In - 500 ppm Bi alloy (b)
Zn - 40 ppm Al - 500 ppm In - 500 ppm Bi
Zn - 70 ppm Al - 500 ppm In - 500 ppm Bi
Zn - 30 ppm Al - 500 ppm In - 1000 ppm Bi
Zn - 40 ppm Al - 500 ppm In - 1000 ppm Bi
Zn - 70 ppm Al - 500 ppm In - 1000 ppm Bi
Zn - 40 ppm Al - 500 ppm In - 2300 ppm Bi
Zn - 70 ppm Al - 500 ppm In - 2300 ppm Bi
Zn - 70 ppm Al - 500 ppm In - 3000 ppm Bi
Zn - 20 ppm Al - 500 ppm In - 1000 ppm Bi
Zn - 40 ppm Al - 500 ppm In - 1000 ppm Bi - 50 ppm Pb
Zn - 70 ppm Al - 500 ppm In - 1000 ppm Bi - 50 ppm Pb

Zn - 40 ppm Al - 500 ppm In - 500 ppm Bi - 50 ppm Pb

Zn - 70 ppm Al - 500 ppm In - 500 ppm Bi - 50 ppm Pb

Zn - 40 ppm Al - 250 ppm In - 250 ppm Bi - 100 ppm Pb

Zn - 250 ppm Li - 250 ppm Bi

Zn - 430 ppm Li - 250 ppm Bi

Zn - 30 ppm Li - 250 ppm Bi - 100 ppm Pb

Zn - 50 ppm Li - 250 ppm Bi - 250 ppm Pb

Zn - 30 ppm Li - 500 ppm Bi

Zn - 50 ppm Li - 500 ppm Bi

Zn - 250 ppm Li - 500 ppm Bi

Zn - 430 ppm Li - 500 ppm Bi

Zn - 50 ppm Li - 500 ppm Bi - 200 ppm Ca

Zn - 250 ppm Li - 500 ppm Bi - 100 ppm Ca

Zn - 30 ppm Li - 500 ppm In

Zn - 50 ppm Li - 500 ppm In

Zn - 250 ppm Li - 500 ppm In

Zn - 430 ppm Li - 500 ppm In

Zn - 50 ppm Li - 500 ppm In - 200 ppm Ca

Zn - 250 ppm Li - 500 ppm In - 100 ppm Ca

Zn - 250 ppm Li - 1000 ppm In

Zn - 430 ppm Li - 1000 ppm In

Zn - 50 ppm Li - 1000 ppm In - 200 ppm Ca

Zn - 250 ppm Li - 2300 ppm Bi

Zn - 430 ppm Li - 2300 ppm Bi

Zn - 50 ppm Li - 3000 ppm Bi

Zn - 30 ppm Li - 3000 ppm Bi

Zn - 50 ppm Li - 2300 ppm Bi - 200 ppm Ca

Zn - 250 ppm Li - 250 ppm Bi - 500 ppm In

Zn - 430 ppm Li - 250 ppm Bi - 500 ppm In

Zn - 30 ppm Li - 250 ppm Bi - 500 ppm In - 100 ppm Pb

Zn - 50 ppm Li - 250 ppm Bi - 500 ppm In - 250 ppm Pb

Zn - 30 ppm Li - 500 ppm Bi - 500 ppm In

Zn - 50 ppm Li - 500 ppm Bi - 500 ppm In

Zn - 250 ppm Li - 500 ppm Bi - 500 ppm In

Zn - 430 ppm Li - 500 ppm Bi - 500 ppm In

Zn - 50 ppm Li - 500 ppm Bi - 500 ppm In - 200 ppm Ca

Zn - 250 ppm Li - 500 ppm Bi - 500 ppm In - 100 ppm Ca

Zn - 30 ppm Li - 1000 ppm Bi - 500 ppm In

Zn - 50 ppm Li - 1000 ppm Bi - 500 ppm In
Zn - 250 ppm Li - 1000 ppm Bi - 500 ppm In
Zn - 430 ppm Li - 1000 ppm Bi - 500 ppm In
Zn - 30 ppm Al - 30 ppm Li - 250 ppm Bi
Zn - 30 ppm Al - 50 ppm Li - 250 ppm Bi
Zn - 70 ppm Al - 30 ppm Li - 250 ppm Bi
Zn - 70 ppm Al - 50 ppm Li - 250 ppm Bi
Zn - 30 ppm Al - 30 ppm Li - 250 ppm Bi - 180 ppm Ca
Zn - 70 ppm Al - 30 ppm Li - 250 ppm Bi - 250 ppm Ca
Zn - 30 ppm Al - 250 ppm Li - 250 ppm Bi
Zn - 70 ppm Al - 250 ppm Li - 250 ppm Bi
Zn - 30 ppm Al - 50 ppm Li - 250 ppm Bi - 180 ppm Pb
Zn - 70 ppm Al - 30 ppm Li - 250 ppm Bi - 250 ppm Pb
Zn - 30 ppm Al - 30 ppm Li - 500 ppm Bi
Zn - 30 ppm Al - 50 ppm Li - 500 ppm Bi
Zn - 70 ppm Al - 50 ppm Li - 500 ppm Bi
Zn - 30 ppm Al - 250 ppm Li - 500 ppm Bi
Zn - 30 ppm Al - 30 ppm Li - 1000 ppm Bi
Zn - 30 ppm Al - 250 ppm Li - 1000 ppm Bi
Zn - 70 ppm Al - 30 ppm Li - 1000 ppm Bi
Zn - 30 ppm Al - 250 ppm Li - 2300 ppm Bi
Zn - 70 ppm Al - 30 ppm Li - 2300 ppm Bi
Zn - 70 ppm Al - 50 ppm Li - 3000 ppm Bi
Zn - 30 ppm Al - 50 ppm Li - 250 ppm In
Zn - 70 ppm Al - 50 ppm Li - 250 ppm In
Zn - 30 ppm Al - 30 ppm Li - 500 ppm In
Zn - 70 ppm Al - 30 ppm Li - 500 ppm In
Zn - 30 ppm Al - 30 ppm Li - 250 ppm In - 250 ppm Bi
Zn - 30 ppm Al - 50 ppm Li - 250 ppm In - 250 ppm Bi
Zn - 70 ppm Al - 30 ppm Li - 250 ppm In - 250 ppm Bi
Zn - 30 ppm Al - 250 ppm Li - 250 ppm In - 250 ppm Bi
Zn - 30 ppm Al - 30 ppm Li - 500 ppm In - 250 ppm Bi
Zn - 30 ppm Al - 50 ppm Li - 500 ppm In - 250 ppm Bi
Zn - 70 ppm Al - 30 ppm Li - 500 ppm In - 250 ppm Bi
Zn - 30 ppm Al - 250 ppm Li - 500 ppm In - 250 ppm Bi
Zn - 30 ppm Al - 50 ppm Li - 500 ppm In - 500 ppm Bi
Zn - 30 ppm Al - 250 ppm Li - 500 ppm In - 500 ppm Bi
Zn - 70 ppm Al - 50 ppm Li - 500 ppm In - 500 ppm Bi

Zn - 30 ppm Al - 30 ppm Li - 500 ppm In - 1000 ppm Bi

Zn - 30 ppm Al - 250 ppm Li - 500 ppm In - 1000 ppm Bi

Zn - 70 ppm Al - 30 ppm Li - 500 ppm In - 1000 ppm Bi

Zn - 70 ppm Al - 50 ppm Li - 500 ppm In - 1000 ppm Bi

Zn - 30 ppm Al - 50 ppm Li - 500 ppm In - 2300 ppm Bi

Zn - 70 ppm Al - 30 ppm Li - 500 ppm In - 2300 ppm Bi

Zn - 70 ppm Al - 30 ppm Li - 500 ppm In - 3000 ppm Bi

These powders contain, besides zinc and unavoidable impurities, only the given additives. Unavoidable impurities are the impurities which are present in the zinc and in the additives.

CLAIMS

1. An aluminium-bearing zinc powder for alkaline batteries, characterized in that it consists of 1-95 ppm aluminium and
either, of one of 0.001-2% bismuth, 0.005-2% indium and 0.003-2% lead, and optionally of 0.003-2% calcium ;
or, of 0.001-2% bismuth, of 0.005-2% indium, and optionally of 0.003-2% lead ;
or, of one of 0.001-2% bismuth and 0.005-2% indium, of 0.003-2% lead, and optionally 0.003-2% calcium ;
and for the rest of zinc and the unavoidable impurities present in the aforesaid metals, being excluded the indium-bearing powders with 50 ppm aluminium unless these powders contain calcium.

2. A lithium-bearing zinc powder for alkaline batteries, characterized in that it consists of 1-1000 ppm lithium and
either, of at least one of 0.001-2% bismuth and 0.005-2% indium, and optionally of 0.003-2% calcium ;
or, of 0.003-2% lead, of 0.003-2% calcium, and optionally of 0.005-2% indium ;
or, of 0.001-2% bismuth, of 0.003-2% lead, and optionally of at least one of 0.005-2% indium and 0.003-2% calcium ;
and for the rest of zinc and the unavoidable impurities present in the aforesaid metals.

3. An aluminium- and lithium-bearing zinc powder for alkaline batteries, characterized in that it consists of 1-95 ppm aluminium, of 1-1000 ppm lithium, of at least one of 0.001-2% bismuth, 0.005-2% indium and 0.003-2% lead, and optionally of 0.003-2% calcium, and for the rest of zinc and the unavoidable impurities present in the aforesaid metals.

4. A powder according to claim 1 of 3, characterized in that it contains 1-85 ppm Al.

5. A powder according to claim 4, characterized in that it contains 1-45 ppm Al.

6. A powder according to claim 5, characterized in that it contains 5-45 ppm Al.

7. A powder according to one of the claims 2-6, characterized in that it contains 5-500 ppm Li.

8. A powder according to claim 7, characterized in that it contains 10-200 ppm Li.

9. A powder according to one of the claims 1-8, characterized in that it contains 0.003-0.3% Bi.

10. A powder according to claim 9, characterized in that it contains 0.003-0.2% Bi.

11. A powder according to claim 10, characterized in that it contains 0.003-0.1% Bi.

12. A powder according to one of the claims 1-11, characterized in that it contains only Bi and at least one of Al and Li as alloying elements.

13. A powder according to one of the claims 1-11, characterized in that it contains only Bi, Ca and at least one of Al and Li as alloying elements.

14. A powder according to one of the claims 1-11, characterized in that it contains only In. Bi and at least one of Al and Li as alloying elements.

15. A powder according to one of the claims 1-11, characterized in that it contains only Bi, In, Li, Ca and optionally Al as alloying elements.

16. A powder according to one of the claims 1-11, characterized in that it contains only Pb, Bi and at least one of Al and Li as alloying elements.

17. A powder according to one of the claims 1-11, characterized in that it contains only Pb, Bi, Ca and at least one of Al and Li as alloying elements.

18. A powder according to one of the claims 1-11, characterized in that it contains only Pb, Bi, In and at least one of Al and Li as alloying elements.

19. A powder according to one of the claims 1-11, characterized in that it contains only Pb, Bi, In, Li, Ca and optionally Al as alloying elements.

20. A powder according to one of the claims 1-11, 14, 15, 18 and 19, characterized in that it contains 0.01-0.1% In.

21. A powder according to one of the claims 1-11 and 16-19, characterized in that it contains 0.01-0.1% Pb.

22. A powder according to one of the claims 1-11, 13, 15, 17 and 19, characterized in that it contains 0.005-0.1% Ca.

23. Alkaline battery containing an anode, a cathode and an electrolyte, characterized in that the anode contains as active material a powder according to one of the claims 1-22.

24. Alkaline battery according to claim 23, characterized in that the powder contains metals cemented from the electrolyte.

INTERNATIONAL SEARCH REPORT

Inte. ...ional Application No
PCT/EP 94/00449

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C22C18/00 H01M4/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C22C H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 457 354 (MATSUSHITA ELECTRIC INDUSTRIAL) 21 November 1991 cited in the application see table 3	1,5,6, 9-11,23
X	EP,A,0 384 975 (VARTA) 5 September 1990 cited in the application see claims 1-5	2,7-11, 18,20, 21,23
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 87-254043 & JP,A,62 176 053 (MITSUI MINING & SMELTING) 1 August 1987 cited in the application see abstract	3-8,20, 23

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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2

Date of the actual completion of the international search	Date of mailing of the international search report
22 April 1994	04. 05. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ashley, G

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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2

INTERNATIONAL SEARCH REPORT

Int. ..tional Application No
PCT/EP 94/00449

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		JP-A-	4026066	29-01-92
		JP-A-	4026067	29-01-92
		AU-B-	622588	09-04-92
		AU-A-	7701791	28-11-91
		CA-A-	2042549	18-11-91
		US-A-	5168018	01-12-92
EP-A-0384975	05-09-90	DE-A-	3902650	02-08-90
		DE-D-	58905395	30-09-93
		ES-T-	2044040	01-01-94
		US-A-	4994333	19-02-91
EP-A-0427315	15-05-91	BE-A-	1003415	17-03-92
		AU-B-	625011	25-06-92
		AU-A-	6588290	16-05-91
		CA-A-	2029436	11-05-91
		JP-A-	3173731	29-07-91
		US-A-	5082622	21-01-92